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Fused thiabenzene oxide, 2-methyl-4-methylthiobenzo[*b*]thieno[3,2-*c*]thiapyran 2,5,5-trioxide (**2**) was synthesized by the reaction of 2,3-dihydro-2-bis(methylthio)methylene-3-oxobenzo[*b*]thiophene 1,1-dioxide (**1**) with trimethyl sulfoxonium iodide in the presence of sodium hydride in tetrahydrofuran. Similarly, fused azathiabenzene oxide, 2-methyl-4-methylthiobenzo[*b*]thieno[2,3-*c*][1,2]thiazine 2,5,5-trioxide (**3**) was prepared from **1** and sulfoximine in good yield.

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It is well known that a bis(methylthio)methylene functional group on heterocyclic compounds [1-13] is very useful for the preparation of heterocyclic compounds like ketene dithioacetals [14-21]. In recent years, the synthesis of monocyclic 1-methylthiabenzene 1-oxides and 1-methyl-2-azathiabenzene 1-oxides by the reaction of ketene dithioacetal has been reported by Furukawa [22], Rudolf [23,24], and others [25]. Despite the numerous reports concerning the utility of bis(methylthio)methylene heterocyclic compounds in the synthesis of heterocycles, to the best of our knowledge, the reaction of these compounds with *S*-ylides has never been investigated. The present investigation of 2,3-dihydro-2-bis(methylthio)methylene-3-

oxobenzo[*b*]thiophene 1,1-dioxide (**1**) was undertaken in order to prepare the heterocyclic fused thiabenzene oxide and their aza analogues, which are new classes of thiabenzenes.

The reaction of **1** with trimethylsulfoxonium iodide in the presence of sodium hydride under reflux in tetrahydrofuran for 4 hours gives thiabenzene oxide, **3**, 2-methyl-4-methylthiobenzo[*b*]thieno[3,2-*c*]thiapyran 2,5,5-trioxide, in 21% yield.

Treatment of an *N*-substituted dimethyl sulfoximine, 2,3-dihydro-2-( $\alpha$ -methylthio- $\alpha$ -dimethylsulfoximino)methylene-3-oxobenzo[*b*]thiophene 1,1-dioxide (**5**), which was prepared by the reaction of **1** with dimethylsulfoximine, with sodium hydride in tetrahydrofuran afforded an azathiabenzene oxide, 2-methyl-4-methylthiobenzo[*b*]thieno[2,3-*c*][1,2]thiazine 2,5,5-trioxide (**6**), in 61% yield. When **1** was reacted with excess dimethylsulfoximine at 130° to give 2,3-dihydro-2-[bis(dimethylsulfoximino)methylene]-3-oxobenzo[*b*]thiophene 1,1-dioxide (**7**) in 73% yield. Compound **7** was also treated with sodium hydride in a manner similar to that used for the preparation of **6** from **5** to give **8** in 90% yield.

## EXPERIMENTAL

All melting points were determined in a capillary tube and are uncorrected. Infrared (ir) spectra were recorded in potassium bromide pellets on a JACO IRA-2 spectrometer, ultraviolet (uv) absorption spectra were determined in 95% ethanol on a Hitachi EP-S2 spectrometer, and nuclear magnetic resonance (nmr) spectra were obtained on a JNM-PS-100 (100 MHz) spectrometer with tetramethylsilane as an internal standard. Mass spectra (ms) were recorded on a JEOL JMS-01SG mass spectrometer.

A mixture of 0.57 g (2 mmoles) of **1**, 0.19 g (4 mmoles) of sodium hydride (50% in oil), 1.55 g (8 mmoles) of triethylsulfoxonium iodide (**2**), and 20 ml of anhydrous THF was refluxed for 3 hours. After evaporation of the solvent, 100 ml of water was added to the residue. The precipitate was collected by filtration and recrystallized from methanol to give 0.13 g (21%) of pale yellow leaflets, mp 276° dec; ir (potassium bromide):  $\nu$  max cm<sup>-1</sup> 3060, 3010, 2990, 1540, 1458, 1437, 1262, 1151, 1136; uv (ethanol):  $\lambda$  max nm 216, 262, 270 (sh), 284 (sh), 375; (ethanol):  $\lambda$  min nm 241, 342 (insufficient solubility); ms:  $m/z$  312 (M<sup>+</sup>); <sup>1</sup>H-nmr (DMSO-*d*<sub>6</sub>):  $\delta$  2.54 (3H, s, SMe), 3.76 (3H, s, 2-Me), 6.28 (1H, d, *J* = 4 Hz, 3-H), 6.91 (1H,

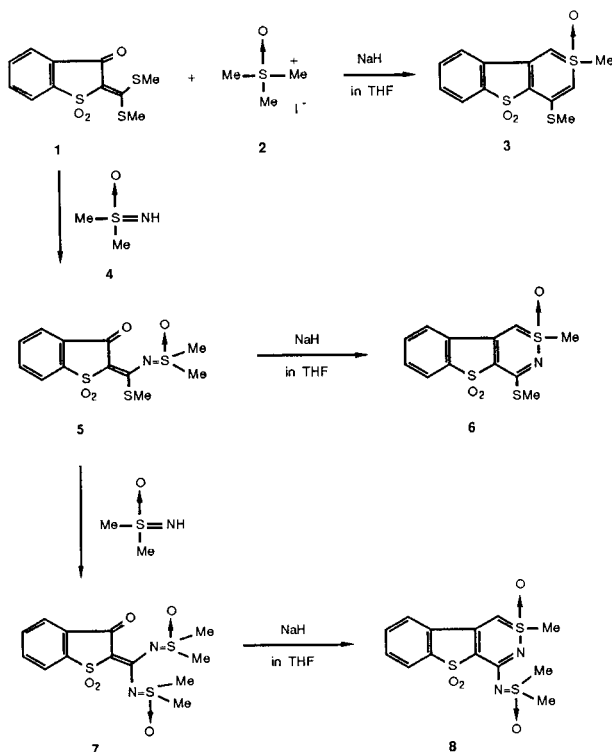


Chart 1

d, J = 4 Hz, 1-H), 7.64-8.04 (4H, m, 6,7,8,9-H).

*Anal.* Calcd. for  $C_{13}H_{12}O_3S_3$ : C, 49.98; H, 3.87; S, 30.79. Found: C, 49.77; H, 3.86; S, 30.73.

2,3-Dihydro-2-( $\alpha$ -methylthio- $\alpha$ -dimethylsulfoximino)methylene-3-oxo[b]thiophene 1,1-Dioxide (**5**).

A solution of 0.57 g (2 mmoles) of **1** and 0.28 g (3 mmoles) of sulfoximine in 50 ml of benzene was refluxed for 1 hour. After evaporation of the solvent, the reaction product was recrystallized from methanol to give 0.62 g (94%) of yellow prisms, mp 204°; ir (potassium bromide):  $\nu$  max  $cm^{-1}$  1654 (CO), 1320 (SO<sub>2</sub>), 1125 (SO<sub>2</sub>); uv (ethanol):  $\lambda$  max nm (log  $\epsilon$ ) 219 (4.30), 260 (4.13), 358 (4.32); <sup>1</sup>H-nmr (deuteriochloroform):  $\delta$  2.68 (3H, s, SMe), 3.47 (6H, s, S-Me), 7.64-8.08 (4H, m, 4,5,6,7-H).

*Anal.* Calcd. for  $C_{12}H_{13}NO_4S_2$ : C, 43.49; H, 3.95; N, 4.23; S, 29.02. Found: C, 43.20; H, 3.99; N, 4.20; S, 28.74.

2-Methyl-4-methylthiobenzo[b]thieno[2,3-d][1,2]thiazine 2,5,5-Trioxide (**6**).

A mixture of 0.66 g (2 mmoles) of **4**, 0.192 g (50% , 4 mmoles) of sodium hydride and 10 ml of anhydrous THF was refluxed for 3 hours, then cooled. The reaction mixture was poured into 100 ml of ice-water. The precipitate was collected by filtration and recrystallized from benzene-methanol to give 0.38 g (61%) of pale yellow plates, mp 282° dec; ir (potassium bromide):  $\nu$  max  $cm^{-1}$  1321 (SO<sub>2</sub>), 1153 (SO<sub>2</sub>); uv (ethanol):  $\lambda$  max nm 225, 242 (sh), 267 (sh), 273, 366; (ethanol):  $\lambda$  min nm 219, 248, 328 (insufficient solubility); <sup>1</sup>H-nmr (DMSO-D<sub>6</sub>):  $\delta$  2.56 (3H, s, SMe), 3.69 (3H, s, 2-Me), 7.48-8.12 (4H, m, 6,7,8,9-H); ms: m/z 313 (M<sup>+</sup>).

*Anal.* Calcd. for  $C_{12}H_{11}NO_3S_3$ : C, 45.99; H, 3.54; N, 4.47; S, 30.69. Found: C, 45.80; H, 3.43; N, 4.45; S, 30.65.

2,3-Dihydro-2-bis(dimethylsulfoximino)methylene-3-oxobenzo[b]thiophene 1,1-Dioxide (**7**).

A mixture of 0.57 g (2 mmoles) of **1** and 0.56 g (6 mmoles) of sulfoximine was heated at 130° for 1 hour, then cooled. The reaction product was recrystallized from methanol to give 0.55 g (73%) of colorless needles, mp 264° dec; ir (potassium bromide):  $\nu$  max  $cm^{-1}$  1645 (CO), 1357 (SO<sub>2</sub>), 1134 (SO<sub>2</sub>); uv (ethanol):  $\lambda$  max nm (log  $\epsilon$ ) 216 (4.43), 251 (4.17), 269 (4.08), 277 (4.17), 350 (4.28); <sup>1</sup>H-nmr (trifluoroacetic acid):  $\delta$  3.65 (12H, s, S-Me), 8.08-8.34 (4H, m, 4,5,6,7-H).

*Anal.* Calcd. for  $C_{13}H_{16}N_2O_5S_3$ : C, 41.48; H, 4.28; N, 7.44; S, 25.55. Found: C, 41.23; H, 4.33; N, 7.44; S, 25.36.

4-Methylsulfoximino-2-methylbenzo[b]thieno[2,3-d][1,2]thiazine 2,5,5-Trioxide (**8**).

This compound was synthesized from **7** in a manner similar to that described for the preparation of **6** from **5**. The yield was 90%. An analytical sample was recrystallized from methanol-benzene to give yellow needles, mp 280° dec; ir (potassium bromide):  $\nu$  max  $cm^{-1}$  1352 (SO<sub>2</sub>), 1143 (SO<sub>2</sub>); methanol-benzene  $\lambda$  max nm 212, 237, 263, 271, 370; (ethanol):  $\lambda$  min nm 233, 243, 267, 331 (insufficient solubility); <sup>1</sup>H-nmr (DMSO-D<sub>6</sub>):  $\delta$  3.52 (6H, s, SMe), 3.57 (3H, s, 2-Me), 6.81 (1H, s, 1-H), 7.64-8.04 (4H, m, 6,7,8,9-H); ms: m/z 358 (M<sup>+</sup>).

*Anal.* Calcd. for  $C_{13}H_{14}N_2O_4S_2$ : C, 43.56; H, 3.94; N, 7.81; S, 26.83. Found: C, 43.40; H, 3.84; N, 7.74; S, 26.57.

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